

International application No. PCT/SE 99/00086

INTERNATIONAL SEARCH REPORT Information on patent family members

02/03/99

International application No.
PCT/SE 99/00086

Patent document cited in search report			Publication date		Patent family member(s)	Publication date
EP	0306972	A1	15/03/89	SE DE	0306972 T3 3871668 A	09/07/92
				FI JP	884135 A 1103684 A	11/03/89 20/04/89
 US	4647392	A	03/03/87	CA EP SE	1258162 A 0229440 A,B 0229440 T3	08/08/89 22/07/87
				JP	62158778 A	14/07/87





REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only	
PCT/SE 9 9 / 0 0 0 8 6 International Application No.	
2 1 -01- 1999 2 2 -01- 1999	
The Swedish Patent Office PCT International Application	
Name of receiving Office and "PCT International Application"	

Applicant's or agent's file reference (if desired) (12 characters maximum) P15409PC/SC Box No. 1 TITLE OF INVENTION Frost resistant heating/cooling fluid Box No. II **APPLICANT** Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.) This person is also inventor. ASPEN PETROLEUM AB Telephone No. Sjöportsgatan 2 S-417 64 GOTEBORG Facsimile No. Sweden Teleprinter No. State (i.e. country) of residence: Sweden State (i.e country) of nationality: Sweden all designated States except This person is applicant all designated the United States the States indicated in States the United States of America for the purposes of: of America only the Supplemental Box Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S) Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.) This person is: applicant only STARZMANN, Martin Skårsgatan 68 S-412 69 GOTEBORG applicant and inventor Sweden inventor only (If this check-box is marked, do not fill in below.) State (i.e. country) of residence: State (i.e country) of nationality: Sweden Sweden This person is applicant all designated all designated States except the United States the States indicated in for the purposes of: the United States of America of America only the Supplemental Box Further applicants and/or (further) inventors are indicated on a continuation sheet. Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE The person identified below-is-hereby/has been appointed to act on behalf agent 2 common representative of the applicant(s) before the competent International Authorities as: Name and address: (Family name followed by given name; for a legal entity, full official designation.

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ASSADI, Behdad; EGEROD, Lisbeth; HAMMOND, Andrew; HOLM, Telephone No. 46-31-507700 Ulf; INGER, Ulf; OLSSON, Stefan; SPINOSO de CABERO, Adriana; Facsimile No. ROTH-SCHRAMM, Carina; ROTH, Eva-Stina; ROTH, Michel; WESTMAN 46-31-7790640 Börje of GÜTEBORGS PATENTBYRA DAHLS AB, Sjöporten 4, S-417 64 GÖTEBORG, Sweden Teleprinter No. Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

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Box No. V DESIGNATION OF STATES										
The follow	The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes: at least one must be marked):									
Regional	Regional Patent									
	ARIPO Patent: GH Ghana, GM Gambia KE Kenya, LS	S Le	soi	tho i	MW Malawi SD Sudan SZ Swaziland LIC					
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X EA	Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT									
X EP	European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT									
X OA	OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, Cl Côte d'Ivore, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of PCT (if other kind of protection or treatment desired, specify on dotted line)									
National I	Patent (if other kind of protection or treatment desired spe									
X AL	Albania	\mathbf{K}]	LS	Lesotho					
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X AT		K]	LU	Luxembourg					
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k LK	Sri Lanka									
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Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 moths from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

Form PCT/RO/101 (second sheet) (July 1998)

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Box No. VI PRIORITY C	Y	runner prior		
Filing date of earlier application (day/month/year)	Number of earlier application	national application: country	Where earlier application:* regional application:* regional office	international application: receiving Office
item (1) 22 Jan. 98				
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Box No. VIII CHECK LIST:	LANGUAGE OF FILING	G		
This international application co	s: 1 X fee calcula	l application is accompani	ied by the item(s) market	d below:
request	3 1/2	gned power of attorney		
description (excluding sequence listing part) :	3. copy of ge	eneral power of attorney; re	eference number, if any:	
claims :		explaining lack of signatur	re	
abstract :	1	ocument(s) identified in Bo	` ,	
drawings :	1 –	of international application	, , ,	
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Total number of sheets:	8. nucleotide 9. other (spec	and/or amino acid sequen	ce listing in computer re	adable form
Figure of the drawings which should accompany the abstract:		iguage of filing of the rnational application:		
Box No. IX SIGNATURE	OF APPLICANT OR AGE	ENT		
Next to each signature, indicate the na		capacity in which the person sig	gns (if such capacity is not ob	ovious from reading the request).
Göteborg, 21 ja	nuari 1999			
6. Ox	Wolf !			
Eva-Stina Roth GÖTEBORGS PATEN	/ TBYRÅ DAHLS AB			
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Date of actual receipt of the international application:	purported	2 1 -01- 1999		2. Drawings:
Corrected date of actual rece timely received papers or dra the purported international a	awings completing	2 2 -01- 1999		received:
4. Date of timely receipt of the corrections under PCT Artic				not received:
5. International Searching Auth (if two or more are competer	. ISA/ LE		al of search copy delayed th fee is paid	
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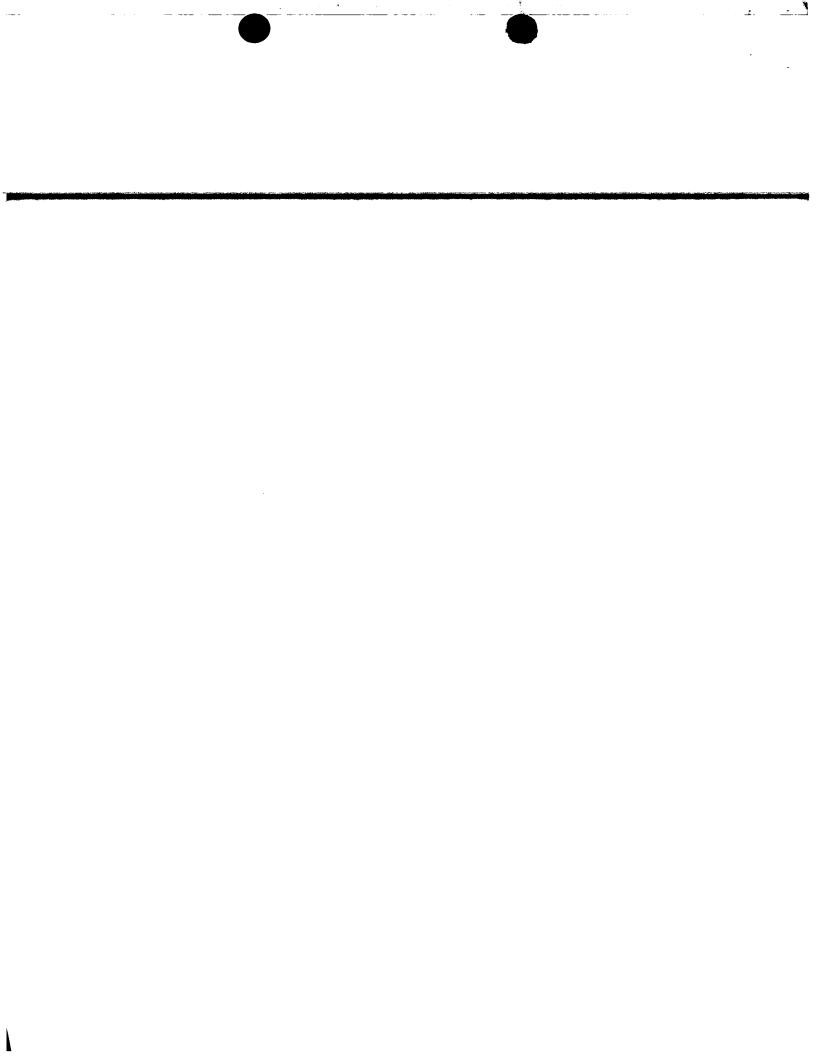
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Date of receipt of the record copy

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Frostresistent värme/kylfluid

Tekniskt område

Föreliggande uppfinning avser en frostresistent vattenhaltig värme/kylfluid innehållande alkalisalter av ättiksyra och/eller myrsyra. Värme/kylfluiden är avsedd för transport av kyla eller värme i industriella kylanläggningar, kylsystem i fartyg och fordon, kylsystem för skridskois i sportanläggningar, värmeväxlare, fjärrvärmesystem, värmepumpar, solfångare etc.

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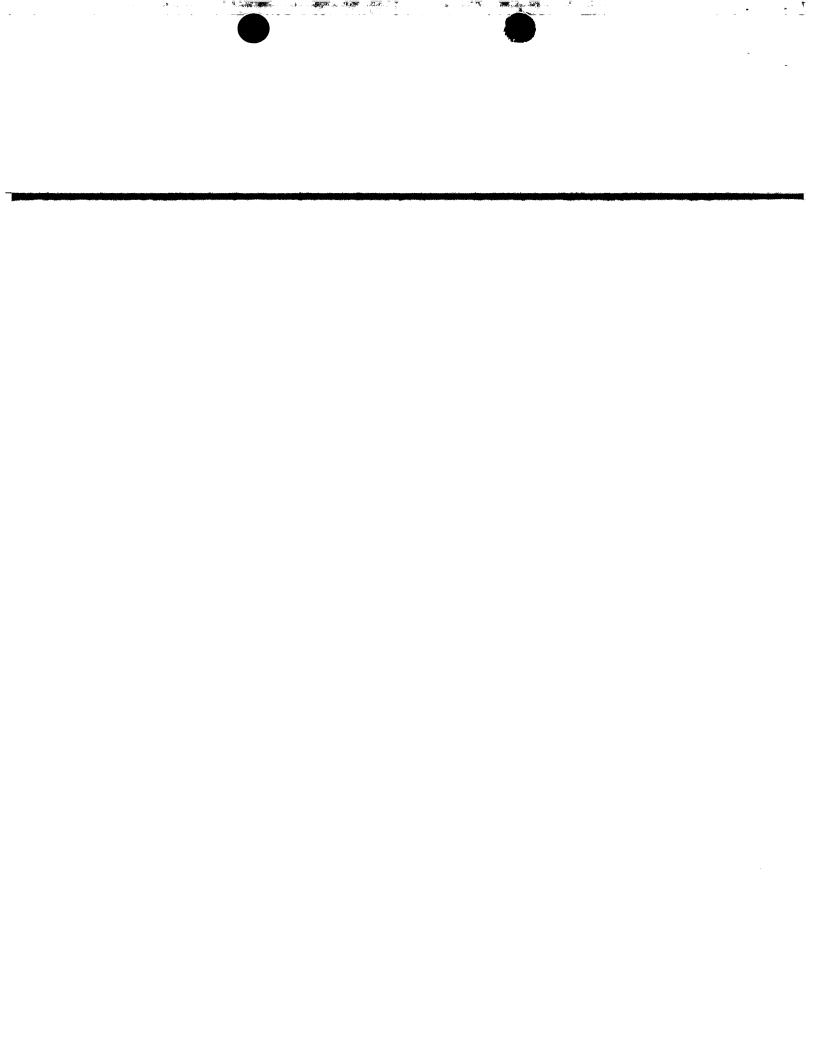
Uppfinningens bakgrund

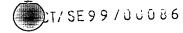
Frostresistens i vattenhaltiga värme/kylfluider erhålls vanligen genom tillsats av etylenglykol. Etylenglykol är en vätska som är obegränsat blandbar med vatten, den uppvisar låg brand- och explosionsrisk och är frostresistent samt färg- och luktlös. Den lägsta stelningspunkten (-57°C) hos en glykol-vattenblandning har man vid en etylenglykolhalt på 60 volyms-%. Nackdelen med etylenglykol är emellertid dess höga giftighet. Därmed utgör den ett miljöhot om den hamnar i hav, sjöar och vattendrag, exempelvis om kylvätska släpps eller läcker ut.

Genom EP-B-0 306 972 är en helt eller delvis glykolfri frostresistent vattenhaltig kylfluid känd, vilken innehåller en tillsats av natriumacetat och natriumformiat eller kaliumacetat och kaliumformiat i vissa mängdförhållanden. Man kan med denna fluidkomposition uppnå en frystemperatur på -70°C eller lägre. Fluidkompositionen uppvisar samtliga fördelar med den konventionella glykol-vattenblandningen, samtidigt som den inte uppvisar dennas giftighet.

Den ovan angivna kylfluiden innehåller emellertid starka joner varvid det är mycket viktigt att ha ett gott korrosionsskydd. I EP-B-0 306 972 beskrivs att man som korrosionsskydd använder bensoesyra, natriumbensoat, kaliumbensoat eller bensotriazol. Dessa är filmbildande kemikalier. Den bildade filmen skyddar metallytor från korrosionsangrepp. Filmskiktet måste vara intakt över hela metallytan för att inte







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riskera lokala korrosionsangrepp. En nackdel med filmen är en försämrad värmeöverföring mellan metallytan och kylfluiden.

Uppfinningens ändamål och viktigaste kännetecken
Ändamålet med föreliggande uppfinning är att erbjuda en korrosionsskyddad
värme/kylfluid av det inledningsvis nämnda slaget vilken uppvisar en hög
värmeöverföring mellan metallyta och fluid samtidigt som korrosionsskyddet är gott.
Detta har uppnåtts genom att den innehåller en korrosionsinhibitor i form av en
blandning av en C₅-C₁₆ monokarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra, en C₅-C₁₆ dikarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra samt en triazol.

Halten alkalisalter av ättiksyra och/eller myrsyra i värme/kylfluiden bör företrädesvis vara mellan 5 och 50 vikts-% räknat på fluidens totala vikt.

Värme/kylfluiden innehåller mellan 0,4 och 10 vikts-% företrädesvis mellan 0,5 och 2 vikts-% av korrosionsinhibitorn enligt ovan räknat på den totala vikten av alkalisalterna av ättiksyra och/eller myrsyra.

Beskrivning av uppfinningen

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Det är genom ovan nämnda EP-B-0 306 972 känt att tillsats av alkalisalter av vissa anjoner, huvudsakligen acetater och formiater, till vatten resulterar i en kraftig fryspunktssänkning av ett vattenhaltigt medium. Fryspunktssänkningen blir speciellt stor vid vissa blandningsförhållanden av de ingående salterna.

Värme/kylfluiden enligt uppfinningen innehåller mellan 5 och 50 vikts-% alkalisalter av ättiksyra och/eller myrsyra räknat på fluidens vikt, framför allt natriumacetat, kaliumacetat, natriumformiat och/eller kaliumformiat. De ingående salterna kan förekomma i alla inbördes blandningsförhållanden, dvs. enbart ett av salterna eller två eller flera salter i blandning med varandra. Beroende dels på den totala salthalten och

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dels på salternas blandningsförhållanden erhålls olika fryspunktssänkning för fluiden. I fluiden kan även ingå andra fryspunktsnedsättande tillsatser, t ex urea.

Värme/kylfluiden enligt uppfinningen är en stark jonlösning varvid betydelsen av ett effektivt korrosionsskydd är extra stor. I EP-B-0 306 972 beskrivs tillsats av en korrosionsinhibitor i form av bensoesyra, natriumbensoat, kaliumbensoat eller bensotriazol, vilka är filmbildande kemikalier som skapar en skyddande film på metallytor och därmed skyddar dem från korrosionsangrepp. Som omtalats ovan är nackdelarna med denna typ av korrosionsinhibitorer dels att filmskiktet måste vara intakt över hela metallytan för att korrosionsskyddet skall bli effektivt och lokala korrosionsangrepp undvikas och dels att värmeöverföringen mellan metallyta och värme/kylfluid försämras.

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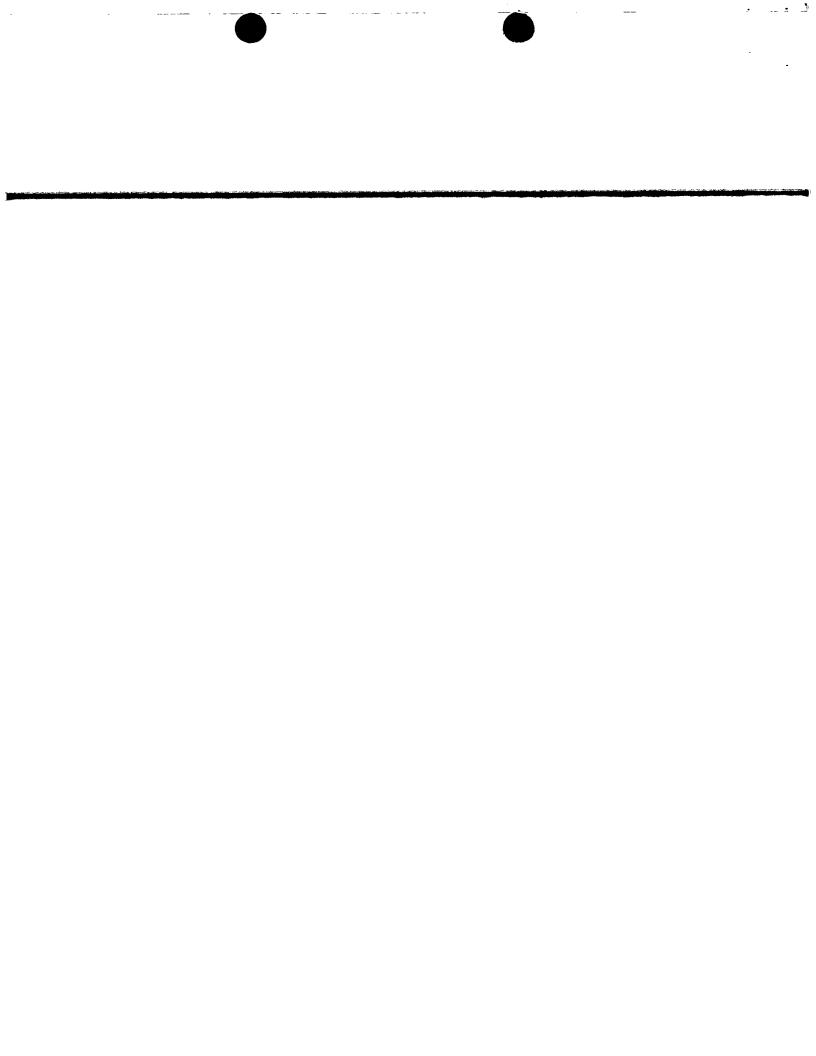
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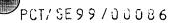
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Det har nu enligt uppfinningen överraskande visat sig att en tillsats en korrosionsinhibitor i form av en blandning av en C_5 - C_{16} monokarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra, en C_5 - C_{16} dikarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra samt en triazol förutom ett fullgott korrosionsskydd även ger en mycket bra värmeöverföring mellan metallyta och fluid.

- En korrosionsinhibitor av detta slag finns beskriven i US-A-4,647,392. Korrosionsinhibitorn är enligt nämnda referens avsedd att användas i glykol-vattenblandningar.

 Användning som korrosionsinhibitor i saltlösningar av det slag som uppfinningen avser
 finns dock inte antytt i det amerikanska patentet.
- Mängden av de i korrosionsinhibitorn ingående komponenterna kan variera mellan 0,02 och 3 vikts-% räknat på fluidens vikt för vardera av monokarboxylsyran och dikarboxylsyran eller alkali-, ammonium- eller aminsalterna av sagda syra. Mängden triazol kan variera mellan 0,02 och 2 vikts-% räknat på fluidens totala vikt.
- Den totala halten av korrosionsinhibitorn bör vara mellan 0,4 och 10 vikts-% företrädesvis mellan 0,5 och 2 vikts-% räknat på fluidens vikt.





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Korrosionsinhibitorn innefattar en blandning av tre huvudkomponenter, nämligen en monokarboxylsyra, en dikarboxylsyra och en triazol. Monokarboxylsyran är företrädesvis en alifatisk C_5 - C_{16} monokarboxylsyra, företrädesvis vald från gruppen oktansyra, nonansyra, dekansyra, undekansyra eller dodekansyra , 2-etylhexansyra och neodekansyra.

Dikarboxylsyran är företrädesvis antingen en C_8 - C_{12} alifatisk dikarboxylsyra vald från gruppen suberinsyra, azealinsyra, sebacinsyra, undekandisyra, dodekandisyra och disyran av dicyklopentandien eller en C_8 - C_{12} aromatisk dikarboxylsyra, företrädesvis tereftalsyra.

Triazolen är företrädesvis tolyoltriazol eller bensoetriazol.

15 Kombinationen av mono- och dikarboxylsyra eller dess salter ger en synergistisk effekt vad beträffar korrosionsskydd av metallytor jämfört med användning av enbart den ena typen av syra. Triazolen används specifikt som kopparskydd.

Andra konventionella korrosionshämmande komponenter kan naturligtvis även ingå i värme/kylfluiden enligt uppfinningen

Exempel

För att testa värmeöverföringskaraktäristik användes ett system där vätska som skall testas cirkulerar med ett konstant volymflöde och under konstant tryck. Denna vätska passerar en metallkupong på vilken en värmningsanordning är applicerad. Vätskans temperatur hålles konstant med hjälp av en kylslinga. Metallkupongens temperatur mäts och registreras över tiden. En ökning av temperaturen i metallkupongen visar en relativ försämring i värmeöverföringsförmågan över samma tid

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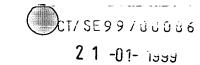
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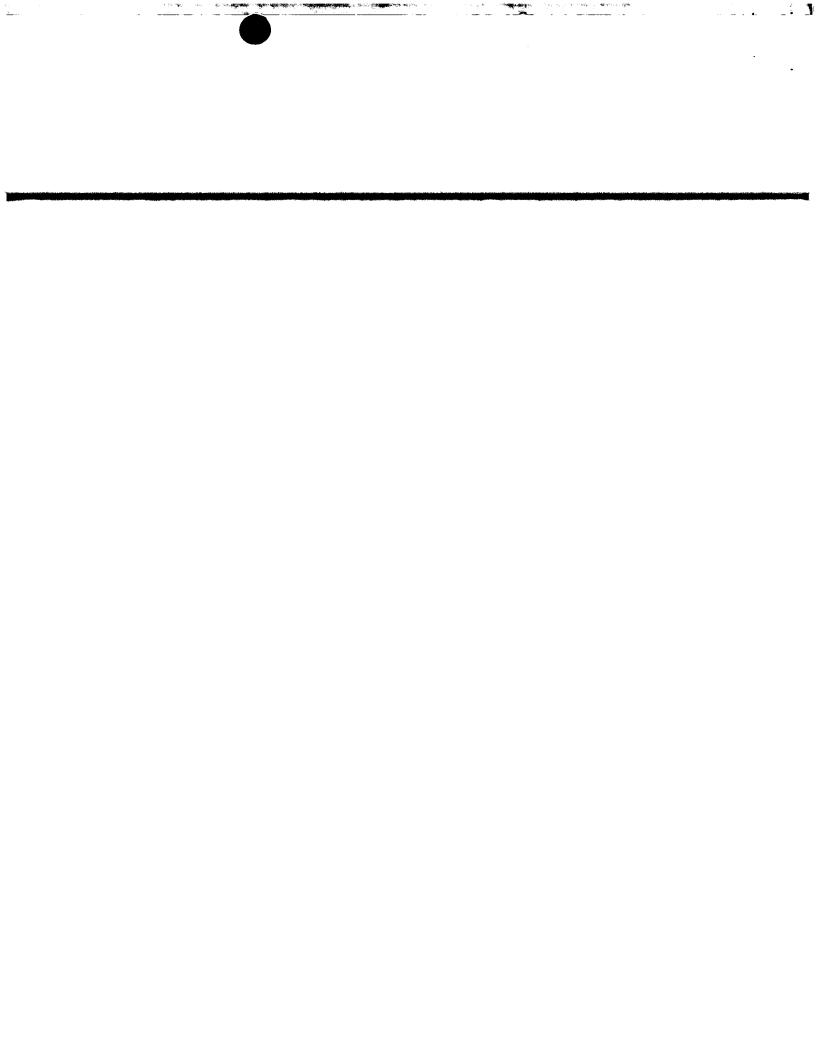
De testade vätskorna uppvisade följande sammansättning:

INGÅENDE KOMPO- NENT (vikts-%)	Referens - Kylfluid med konventionell inhibitor	Test - Kylfluid med inhibitor enligt uppfinningen
Vatten	49,8	60
Kaliumacetat	31,2	31,2
Kaliumformiat	7,8	7,8
Natriumbensoat	1,1	-
Tolytriazol	1,7	-
Borax	0,3	-
Natriummetafosfat	1	-
Natriumnitrat	1,8	-
Natriumsilikat	0,3	-
Glycerin	5	_
Korrosionsinhibitor enl. uppfinningen	-	1

Följande resultat erhölls beträffande värmeöverföringskaraktäristiken:

20	Testlängd (h)	Referens Kupongtemperatur (°C)	Test Kupongtemperatur (°C)	
	0	170	170	
	10	181	171	
	20	183	171	
	30	184	171,5	
25	40	186	171	
	45	188	171,5	

Som framgår av dessa resultat gav testvätskan, vilken innehöll en tillsats av en korrosionsinhibitor enligt uppfinningen, en mycket liten ökning av temperaturen i metallkupongen över tiden, vilket visar på en bibehållen hög väremöverföring mellan



Patentkrav

1. Frostresistent vattenhaltig värme/kylfluid innehållande alkalisalter av ättiksyra och/eller myrsyra,

k ä n n e t e c k n a d a v att den även innehåller en korrosionsinhibitor i form av en blandning av en C_5 - C_{16} monokarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra, en C_5 - C_{16} dikarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra samt en triazol.

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- 2. Kylfluid enligt patentkrav 1,
- k ä n n e t e c k n a d a v att den innehåller mellan 5 och 50 vikts-% alkalisalter av ättiksyra och/eller myrsyra räknat på fluidens vikt.
- 3. Kylfluid enligt patentkrav 1 eller 2, k ä n n e t e c k n a d a v att den innehåller mellan 0,4 och 10 vikts-% företrädesvis mellan 0,5 och 2 vikts-% av korrosionsinhibitorn räknat på den totala vikten av kylfluiden.
- 4. Kylfluid enligt något eller några av föregående patentkrav,
 k ä n n e t e c k n a d a v att den innehåller mellan 0,02 och 3 vikts-% av
 monokarboxylsyran eller alkali-, ammonium- eller aminsalter av sagda syra räknat på
 den totala vikten av kylfluiden.
- 5. Kylfluid enligt patentkrav 4, kännetecknad av att den innehåller mellan 0,02 och 3 vikts-% av dikarboxylsyran eller alkali-, ammonium- eller aminsalter av sagda syra räknat på den totala vikten av kylfluiden.

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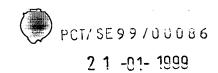
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- 6. Kylfluid enligt patentkrav 4 och 5, k ännet ecknad av att den innehåller mellan 0,02 och 2 vikts-% triazol räknat på den totala vikten av kylfluiden.
- 7. Kylfluid enligt något eller några av föregående patentkrav, k ä n n e t e c k n a d a v att sagda monokarboxylsyra är en alifatisk C₅-C₁₆ monokarboxylsyra, företrädesvis vald från gruppen oktansyra, nonansyra, dekansyra, undekansyra eller dodekansyra, 2-etylhexansyra och neodekansyra.
- 8. Kylfluid enligt något eller några av föregående patentkrav, kännetecknad av att sagda dikarboxylsyra är en C₈-C₁₂ alifatisk dikarboxylsyra vald från gruppen suberinsyra, azealinsyra, sebacinsyra, undekandisyra, dodekandisyra och disyran av dicyklopentandien.
- 9. Kylfluid enligt något eller några av föregående patentkrav,k ä n n e t e c k n a d a v att sagda dikarboxylsyra är en C₈-C₁₂ aromatisk dikarboxylsyra, företrädesvis tereftalsyra.
 - 10. Kylfluid enligt något eller några av föregående patentkrav,
- k ännetecknad av att triazolen är tolyltriazol eller bensotriazol.







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Sammandrag

Frostresistent vattenhaltig värme/kylfluid innehållande alkalisalter av ättiksyra och/eller myrsyra och vilken som korrosionsinhibitor innehåller blandning av en C₅-C₁₆ monokarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra, en C₅-C₁₆ dikarboxylsyra eller alkali-, ammonium- eller aminsalter av sagda syra samt en triazol.



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NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

ASSADI, Behdad Göteborgs Patentbyrå Dahls AB Sjöporten 4 S-417 64 Göteborg SUÈDE

ANKOM

1999 -08- 0 6

Götebergs Patentbyrå Dahls AB

Date of mailing (day/month/year) 29 July 1999 (29.07.99)

Applicant's or agent's file reference

P15409PC/SC

IMPORTANT NOTICE

International application No. PCT/SE99/00086

International filing date (day/month/year) 22 January 1999 (22.01.99)

Priority date (day/month/year) 22 January 1998 (22.01.98)

Applicant

ASPEN PETROLEUM AB et al

Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

AU,CN,EP,IL,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,EA,EE,ES,FI,GB,GE,GH,GM,HR,HU,ID, IS,KE,KG,KZ,LC;LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG, SI,SK,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZW The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the

applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 29 July 1999 (29.07.99) under No. WO 99/37733

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer

J. Zahra

Telephone No. (41-22) 338.83.38

Facsimile No. (41-22) 740.14.35

الأسالية ا

From the INTERNATIONAL BUREAU

PCT

INFORMATION CONCERNING ELECTED OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

To:

ASSADI, Behdad Göteborgs Patentbyrå Dahls AB

Sjöporten 4 S-417 64 Göteborg SUÈDE ANKOM

1999 -10- 25

Göteborgs Patentbyrå Dahls A

Date of mailing (day/month/year)

19 October 1999 (19.10.99)

Applicant's or agent's file reference

P15409PC/SC

IMPORTANT INFORMATION

International application No. PCT/SE99/00086

International filing date (day/month/year)

Priority date (day/month/year)

22 January 1999 (22.01.99)

22 January 1998 (22.01.98)

Applicant

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ASPEN PETROLEUM AB et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP:GH,GM,KE,LS,MW,SD,SZ,UG,ZW

EP:AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE

National :AU,BG,BR,CA,CN,CZ,DE,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US :

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA:AM,AZ,BY,KG,KZ,MD,RU,TJ,TM

OA:BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG

National :AL,AM,AT,AZ,BA,BB,BY,CH,CU,DK,EE,ES,FI,GB,GE,GH,GM,HR,HU,ID,IS,

KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MW,MX,PT,SD,SG,SI,SL,TJ,TM,TR,TT,

UA,UG,UZ,VN,YU,ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer:

Jean-Marie McAdams

TAP

Facsimile No. (41-22) 740.14.35

Telephone No. (41-22) 338.83.38

FATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

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Applicant's or agent's file reference

Assistant Commissioner for Patents United States Patent and Trademark Office Box PCT Washington, D.C.20231 ÉTATS-UNIS D'AMÉRIQUE

Date of mailing (day/month/year)
19 October 1999 (19.10.99)

in its capacity as elected Office

International application No.
PCT/SE99/00086

International filing date (day/month/year)
22 January 1999 (22.01.99)

P15409PC/SC

Priority date (day/month/year)
22 January 1998 (22.01.98)

Applicant

STARZMANN, Martin

1.	The designated Office is hereby notified of its election made:
	X in the demand filed with the International Preliminary Examining Authority on:
	19 August 1999 (19.08.99)
	in a notice effecting later election filed with the International Bureau on:
2.	The election X was
	was not
	made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer

Jean-Marie McAdams

Telephone No.: (41-22) 338.83.38

Facsimile No.: (41-22) 740.14.35

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From the

INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

GÖTEBORGS PATENTBYRA DAHLS Sjöportan 4 S-417 64 Göteborg SUEDE PCT

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NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing (day/month/year)

11. 11. 99

Applicant's or agent's file reference P15409PC/SC

International application No. PCT/SE99/00086

International filing date (day/month/year)

Priority date (day/month/year) 22/01/1998

IMPORTANT NOTIFICATION

22/01/1999

Applicant

ASPEN PETROLEUM AB

- 1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
- 2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
- 3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

Authorized officer

Aperribay, I

European Patent Office D-80298 Munich

Tel. +49 89 2399 - 0 Tx: 523656 epmu d

Fax: +49 89 2399 - 4465

Tel.+49 89 2399-8154



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INTERNATIONAL PRELIMINARY EXAMINATION REPORT



(PCT Article 36 and Rule 70)

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P15409F	PC/SC		FOR FURTHER ACTION	Prelimin	ary Examination Report (Form PCT/IPEA/416)
Internation	al application	No.	International filing date (day/	Priority date (day/month/year)	
PCT/SES	99/00086		22/01/1999		22/01/1998
International C09K5/0		ssification (IPC) or natio	onal classification and IPC		
Applicant					
ASPEN I	PETROLE	UM AB			
		al preliminary examin ed to the applicant ac		pared by this l	nternational Preliminary Examining Authori
2. This l	REPORT c	onsists of a total of 5	sheets, including this co	ver sheet.	
b	een amen	ded and are the basis		ets containing	tion, claims and/or drawings which have rectifications made before this Authority the PCT).
These	e annexes	consist of a total of s	sheets.		
3. This i	eport conta	ains indications relati	ng to the following items:		
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11	☐ Prio	rity			
111	□ Non	-establishment of opi	inion with regard to novelt	y, inventive ste	ep and industrial applicability
iV	☐ Lac	k of unity of invention			
V			ler Article 35(2) with regar is suporting such stateme		eventive step or industrial applicability;
VI	☐ Cer	tain documents cited	l		
VII	☐ Cer	ain defects in the inte	ernational application		
VIII	⊠ Cer	tain observations on t	the international application	on	
Date of sub	mission of t	ne demand	Da	te of completion	of this report
19/08/19	99				1 1. 11. 99
Name and	mailing addr	ess of the international	Au	thorized officer	
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International application No. PCT/SE99/00086

l. Basis	of th	report
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·		Description pages:
	1.	This report has been drawn on the basis of (substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.):

	the report since they do not contain amendments.):												
	Description, pages:												
	1-6		as published										
Claims, No.:													
	1-10		as published										
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		the claims,	Nos.:										
		the drawings,	sheets:										
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4.	Add	litional observation	s, if necessary	y :									
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1.	Stat	tement											
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No: Claims Yes: Claims 1-10 Inventive step (IS) No: Claims Industrial applicability (IA) Yes: Claims 1-10 No: Claims

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/SE99/00086

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

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EXAMINATION REPORT - SEPARATE SHEET

Section V:

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability, Article 33 (1) to (4) PCT; citations and explanations supporting such statement

D1: EP-A-0306972 D2: US-A- 4647392

- 1. The present invention relates to a frost resistant heating/cooling fluid containing alkali salts of acetic acid and /or formic acid and also a corrosion inhibitor in the form of a mixture of
 - a C5-C16 monocarboxylic acid or alkali -, ammonium-, or amino salts of said acid,
 - a C5-C16 dicarboxylic acid or alkali -, ammonium-, or amino salts of said acid, and also a triazole, see present claims 1-10.
- The present application meets the requirements of Article 33 (1) and (2) PCT 2. because the subject-matter of claims 1-10 is novel.
 - D1 discloses also a frost resistant heating/cooling fluid containing alkali salts of acetic acid and /or formic acid, the corrosion inhibitor thereof does not contain a mixture of a C5-C16 monocarboxylic acid or alkali -, ammonium-, or amino salts of said acid and a C5-C16 dicarboxylic acid or alkali -, ammonium-, or amino salts of said acid.
 - D2 discloses a frost resistant heating/cooling fluid on the basis of glycols which does not comprise alkali salts of acetic acid and /or formic acid.
 - The subject-matter of present claims 1-10 is therefore novel.
- 3. The present application meets also the requirements of Article 33 (1) and (3) PCT because the subject-matter of claims 1-10 is also inventive.
 - D1 was considered to represent the closest prior art since it discloses a glycolfree frost resistant heating/cooling fluid containing alkali salts of acetic acid and /or formic acid containing corrosion inhibitors, however the corrosion inhibitor is different.

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EXAMINATION REPORT - SEPARATE SHEET

The problem of the present application may be regarded as to provide a further glycol- free frost resistant heating/cooling fluid with improved heat transfer properties

No indication was given in the prior art that the specific combination of corrosion inhibitors as defined in claim 1 i.e. a mixture of a C5-C16 monocarboxylic acid or alkali -, ammonium-, or amino salts of said acid. a C5-C16 dicarboxylic acid or alkali -, ammonium-, or amino salts of said acid and a triazole in a frost resistant heating/cooling fluid containing alkali salts of acetic acid and /or formic acid could be used to solve this problem.

None of the documents of the search report discloses or suggests a heating/cooling fluid as set out in present claims 1-10 containing alkali salts of acetic acid and /or formic acid comprising such a combination of corrosion inhibitors.

Therefore the presence of an inventive step could be acknowledged for the subject-matter of claims 1-10 vis- à- vis the documents of the search report.

4. The present application meets the requirements of Article 33 (1) and (4) PCT because the subject-matter of claims 1-10 is also industrially applicable.

Section VIII:

Certain observations on the international application

On page 3, line 16 of the description the expression "a C5-C16 dicarboxylic acid or alkali -, ammonium-, or amino salts of said acid," was left out.

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WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :		(11) International Publication Number: WO 99/37733
C09K 5/00	A1	(43) International Publication Date: 29 July 1999 (29.07.99)
(21) International Application Number: PCT/SE99/6 (22) International Filing Date: 22 January 1999 (22.6) (30) Priority Data: 22 January 1998 (22.0) 98 (. p. gor a designates ciates except PETROLEUM AB [SE/SE]; Sjöportsgatan September Series (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): STARZMANN, I [SE/SE]; Skårsgatan 68, S-412 69 Göteborg (SE). (74) Agents: ASSADI, Behdad et al.; Göteborgs Patentbyrå AB, Sjöporten 4, S-417 64 Göteborg (SE).	.01.99 S 	BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, PT, CT, TM), European patent (AM, AZ, BY, KG, PT, CT, TM), European patent (BF, Br, CT, CT, CT, M, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. In English translation (filed in Swedish).

(54) Title: FROST RESISTANT HEATING/COOLING FLUID

(57) Abstract

Frost resistant, aqueous cooling/heating fluid containing alkali salts of acetic acid and/or formic acid and which as a corrosion inhibitor contains a mixture of a C_5 - C_{16} monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, a C_5 - C_{16} dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.

FOR THE PURPOSES OF INFORMATION ONLY

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PCT/SE99/00086

WO 99/37733

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Frost resistant heating/cooling fluid

Technical field

The present invention relates to a frost resistant, aqueous heating/cooling fluid, containing alkali salts of acetic acid and/or formic acid. The heating/cooling fluid is intended for transport of cold or heat in industrial cooling plants, cooling systems in vessels and vehicles, cooling systems for skating ice in sports centres, heat exchangers, district heating systems, heat pumps, solar panels etc.

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Background of the invention

In aqueous heating/cooling fluids, frost resistance is usually obtained by means of an addition of ethylene glycol. Ethylene glycol is a liquid which is mixable with water to any extent, exhibits a low risk of fire and explosion, and is frost resistant and also colourless and odourless. The lowest solidifying point (-57 °C) of a glycol-water mixture is at a ethylene glycol content of 60 volume-%. However, the disadvantage with ethylene glycol is its high degree of toxicity. Thereby, it poses an environmental threat if it ends up in the sea, lakes and streams, for instance, if cooling liquid is discharged or leaks out.

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From EP-B-0 306 972, a partially or completely glycol-free, aqueous cooling fluid is known, which contains an addition of sodium acetate and sodium formate or potassium acetate and potassium formate in certain ratios. By means of this fluid composition, a freezing temperature pf -70 °C or lower can be obtained. The fluid composition exhibits all the advantages with the conventional glycol-water mixture, at the same time as it does not exhibit its toxicity.

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However, the above-mentioned cooling fluid contains strong ions, wherein it is very important to have a good corrosion protection. In EP-B-0 306 972, it is disclosed that benzoic acid, sodium benzoate, potassium benzoate or benzotriazole are used for corrosion

protection. These are film-forming chemicals. The formed film protects metal surfaces from corrosion attacks. In order not to risk local corrosion attacks, the film layer has to be intact across the entire metal surface. A disadvantage with the film is an impaired heat transfer between the metal surface and the cooling fluid.

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Purpose of the invention and most important features

The purpose of the present invention is to provide a corrosion protected heating/cooling fluid of the above-mentioned type, which exhibits an effective heat transfer between metal surface and fluid, at the same time as the corrosion protection is excellent. This has been achieved by means of the fluid containing a corrosion inhibitor in the form of a mixture of a C_5 - C_{16} monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.

The content of alkali salts of acetic acid and/or formic acid in the heating/cooling fluid should preferably be between 5 and 50 weight-%, calculated on the total weight of the fluid.

The heating/cooling fluid contains between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-% of the above-mentioned corrosion inhibitor, calculated on the total weight of the alkali salts of acetic acid and/or formic acid.

Summary of the invention

From the above-mentioned EP-B-0 306 972, it is known that an addition of alkali salts of certain anions, mainly acetates and formates, to water results in a strong depression of freezing-point of an aqueous medium. The depression of freezing-point becomes particularly large at certain mixing ratios of the included salts.

The heating/cooling fluid according to the invention contains between 5 and 50 weight-% alkali salts of acetic acid and/or formic acid calculated on the weight of the fluid, primarily sodium acetate, potassium acetate, sodium formate and/or potassium formate. The included salts can be present in any mutual mixing ratio, i.e. only one of the salts or two or several salts in a mixture together. Partly depending on the total salt content, and partly on the

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mixing ratio of the salts, different depressions of freezing-point of the fluid is obtained. Also other freezing-point depressing additions can be included in the fluid, e.g. urea.

The heating/cooling fluid according to the invention is a strong ionic solution, wherein the significance of an efficient corrosion protection is particularly large. EP-B-0 306 972 discloses an addition of a corrosion inhibitor in the form of benzoic acid, sodium benzoate, potassium benzoate or benzotriazole, which are film-forming chemicals which create a protective film on metals surfaces and thereby protects them from corrosion attacks. As mentioned above, the disadvantages with this type of corrosion inhibitors is partly that the film layer must be intact across the entire metal surface in order to make the corrosion protection effective and to avoid local corrosion attacks, and partly that the heat transfer between metal surface and heating/cooling fluid is impaired.

According to the invention, it has now surprisingly been found that, in addition to an excellent corrosion protection, an addition of a corrosion inhibitor in the form of a mixture of a C₅-C₁₆ monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole, furthermore provides an excellent heat transfer between the metal surface and the fluid.

A corrosion inhibitor of this type is disclosed in US-A-4,647,392. According to this document, the corrosion inhibitor is intended to be used in glycol-water mixtures. The use as a corrosion inhibitor in salt solutions of the type which the invention relates to, however, is not disclosed in the U.S. patent.

The amounts of the components included in the corrosion inhibitor can vary between 0.02 and 3 weight-%, calculated on the weight of the fluid, for both the monocarboxylic acid and the dicarboxylic acid or the alkali-, ammonium-, or amino-salts of said acid. The amount of triazole can vary between 0.02 and 2 weight-%, calculated on the total weight of the fluid.

The total content of the corrosion inhibitor should be between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-%, calculated on the weight of the fluid.

The corrosion inhibitor comprises a mixture of three basic components, namely a monocarboxylic acid, a dicarboxylic acid and a triazole. The monocarboxylic acid is preferably an aliphatic C₅-C₁₆ monocarboxylic acid, preferably selected from the group of octanoic acid, nonaic acid, decanoic acid, undecanoic acid or dodecanoic acid, 2-ethylhexanoic acid and neodecanoic acid.

The dicarboxylic acid is preferably either a C_8 - C_{12} aliphatic dicarboxylic acid selected from the group of suberic acid, azealic acid, sebacic acid, undecanoic di-acid, dodecanoic di-acid and the di-acid of di-cyclopentadienylide or a C_8 - C_{12} aromatic dicarboxylic acid, preferably terephthalic acid.

The triazole is preferably tolyoltriazole or benzotriazole.

In comparison with using only one of the acid types, the combination of mono- and dicarboxylic acid or its salts provides a synergistic effect when the corrosion protection of metallic surfaces is concerned. The triazole is specifically used as a cupper protection.

Other conventional corrosion-inhibiting components can of course also be included in the heating/cooling fluid according to the invention.

Example

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In order to test the heat transfer characteristics, a system in which the liquid which is to be tested is circulating with a constant volume flow under constant pressure was used. This liquid passes a metal coupon onto which a heating device is applied. The temperature of the liquid is kept constant by means of a cooling coil. The temperature of the metal coupon is measured and recorded over time. An increase of the temperature in the metal coupon indicates a relative impairment of the heat transfer ability over the same time.

The liquids which were tested exhibited the following compositions:

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INCLUDED Reference - Cooling fluid Test - Cooling fluid with inhibitor according to the with conventional COMPONENTS invention inhibitor (weight-%) 60 49.8 Water 31.2 31.2 Potassium acetate Potassium formate 7,8 7.8 Sodium benzoate 1.1 1.7 Tolyoltriazole 0.3 Borax Sodium meta-phosphate 1 Sodium nitrate 1.8 Sodium silicate 0.3 5 Glycerol 1 Corrosion inhibitor acc. to the invention

The following results were obtained for the heat transfer characteristics:

20	Test duration (h)	Reference	Reference		
		Coupon temperature (°C)	Coupon temperature (°C)		
	0	170	170		
	10	181	171		
	20	183	171		
	30	184	171.5		
25	40	186	171		
	45	188	171.5		

As is evident from these results, the test liquid, which comprised an addition of a corrosion inhibitor according to the invention, gave a very small increase of the temperature in the

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metal coupon over time, something which indicates a maintained effective heat transfer between the metal surface and the fluid. The reference, however, which contained a conventional corrosion inhibitor essentially in accordance with EP 306,972, exhibited a significant einenease of the temperature in the metal coupon in the course of time and, accordingly, a relative impairment of the heat transfer ability in the same time period.

This difference is thought to be the result of the corrosion inhibitor in the reference fluid forming a film between fluid and metal surface, which impairs the heat transfer. It is presumed that such a film formation, however, does not take place when utilizing the corrosion inhibitor according to the invention.

5 Claims

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- 1. A frost resistant heating/cooling fluid containing alkali salts of acetic acid and/or formic acid.
- characterized in that it also contains a corrosion inhibitor in the form of a mixture of a C₅-C₁₆ monocarboxylic acid or alkali-, ammonium-, or amino-salts of said acid, a C₅-C₁₆ dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.
- 2. A cooling fluid according to claim 1,
 c h a r a c t e r i z e d i n that it contains between 5 and 50 weight-% alkali salts of acetic
 acid and/or formic acid calculated on the weight of the fluid.
 - 3. A cooling fluid according to claim 1 or 2, characterized in that it contains between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-% of the corrosion inhibitor, calculated on the total weight of the cooling fluid.
 - 4. A cooling fluid according to any one or any of the preceding claims, c h a r a c t e r i z e d i n that it contains between 0.02 and 3 weight-% of the monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, calculated on the total weight of the cooling fluid.
 - 5. A cooling fluid according to claim 4, characterized in that it contains between 0.02 and 3 weight-% of the dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, calculated on the total weight of the cooling fluid.
 - 6. A cooling fluid according to claim 4 and 5, characterized in that it contains between 0.02 and 2 weight-% triazole calculated on the total weight of the cooling fluid.

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- 7. A cooling fluid according to any one of any of the preceding claims, c h a r a c t e r i z e d i n that said monocarboxylic acid is an aliphatic C₅-C₁₆ monocarboxylic acid, preferably selected from the group of octanoic acid, nonaic acid, decanoicacid, undecanoicacid or dodecanoicacid, 2-ethyl hexanoicacid and neodecanoicacid.
- 8. A cooling fluid according to any one or any of the preceding claims, characterized in that said dicarboxylic acid is a C₈-C₁₂ aliphatic dicarboxylic acid selected from the group of suberic acid, azealic acid, sebacic acid, undecanoic di-acid, dodecanoic di-acid and the di-acid of di-cyclopentadienylide.
 - 9. A cooling fluid according to any one or any of the preceding claims,
 c h a r a c t e r i z e d i n that said dicarboxylic acid is a C₈-C₁₂ aromatic dicarboxylic acid, preferably terephthalic acid.
 - 10. A cooling fluid according to any one or any of the preceding claims, characterized in that the triazole is tolyoltriazole or benzotriazole.